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AN EQUATION OF STATE FOR GAS MIXTURES. II. A STUDY OF THE METHODS OF COMBINATION OF THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE.

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1. INTRODUCTION.

THE classical method of treating the thermodynamic properties of gas mixtures is to combine from the beginning of the discussion the methods of thermodynamics and statistical mechanics. In this manner van der Waals,[1] and van Laar and Lorenz[2] gave relations for the properties of gas mixtures based on the ideas from which van der Waals' equation of state was derived; and Keyes[3] obtained relations by use of the Keyes[4] equation of state.

Recently there has been proposed another method of approach, which involves the separation of the thermodynamic and statistical treatments until the end of the discussion when the general equations derived by thermodynamic methods are integrated by use of an equation of state for gas mixtures. Some assumption or assumptions are necessary as a starting point for the thermodynamic discussion and Gillespie[5] has shown that general relations for the isothermal variation of certain properties of gas mixtures can be derived from the assumption of Dalton's law of partial pressures at low pressures. De Donder,[6] Van Lerberghe[7] and one of the authors[8] have also treated this problem.

It has been found[9] that two assumptions are required in order to derive expressions for the variation of the thermodynamic properties of gas mixtures with both temperature and pressure. The equations so obtained may be called the general thermodynamic relations since they depend only on the two assumptions and the general laws of thermodynamics. In order to evaluate the partial derivatives which each of these equations contains, it is necessary to have available an equation of state for gas mixtures and such a relation must necessarily depend to a greater or less extent on the methods of statistical mechanics.

In the present paper an equation of state for gas mixtures based on the Beattie-Bridgemen equation of state is considered from the standpoint of the recent experimental data.

2. Previous Investigations.

We are concerned here with the methods that have been proposed for calculating, from data on the pure component gases, the pressure (or volume) of a mixture of gases when the volume (or pressure), temperature and composition are given.

(a) *Simple Additive Relationships.*

There are four additive rules for the treatment of gas mixtures which should be mentioned:

1. *Dalton's law.*[10] This is usually stated: The pressure of a mixture of gases is equal to the sum of the pressures of the component gases existing each by itself at the temperature and in the total volume of the mixture. This may be called the law of the additivity of pressures at constant temperature and volume. It is well known that the law does not hold for the successive additions of portions of a pure gas to a given volume unless the gas follows Boyles' law.

On the basis of Dalton's law, the equation of state of a gas mixture would be obtained by adding the equations of state for the component gases in the following manner:

$$p = f_1(V, T, n_1) + f_2(V, T, n_2) + \cdots \tag{1}$$

In this relation p is the total pressure of the gas mixture; V, T, n_1, n_2, $\cdots$ are the total volume and the temperature of the mixture and the number of moles of the Gases 1, 2, $\cdots$ composing the mixture; and

$$p_i = f_i(V, T, n_i) \qquad i = 1, 2, \cdots$$

are the equations of state of the pure gases.

When applied to ideal gases, Dalton's law gives the result that:

$$p_i = px_i$$

where p is the total pressure of the mixture and x_i the mole fraction of Gas i in the mixture. The product px_i is usually called the "partial pressure."

2. *Gibbs-Dalton law.* From a consideration of vapor pressures, Gibbs[11] proposed a modification of Dalton's law: The pressure of a mixture of gases is equal to the sum of the pressures of the component gases existing each by itself at the temperature and with the same value of its chemical potential as in the mixture. Lurie and Gillespie[12] were the first to make a study of the Gibbs-Dalton law. They pointed out that this law leads to the same expression as Dalton's law, equation (1), for the equation of state of a gas mixture.

3. *Amagat's law.* From a study of his measurements of the compressibilities of oxygen, nitrogen and air, Amagat[13] concluded that: The volume of a mixture of gases is equal to the sum of the volumes of the component gases existing each by itself at the temperature and under the total pressure of the mixture. This may be called the law of the additivity of volumes at constant temperature and pressure. Since volume is an extensive property, Amagat's law evidently holds for the "mixing" of various portions of a real gas each being at the same temperature and pressure.

Amagat's law leads to an equation of state for a gas mixture obtained by adding the equations of state of the component gases in the following manner:

$$V = F_1(p, T, n_1) + F_2(p, T, n_2) + \cdots \tag{2}$$

In this relation V is the total volume of the gas mixture; p, T, n_1, n_2, $\cdots$ are the total pressure and the temperature of the mixture and the number of moles of the Gases 1, 2, $\cdots$ composing the mixture; and

$$V_i = F_i(p, T, n_i) \qquad i = 1, 2, \cdots$$

are the equations of state of the pure gases.

4. *Lewis and Randall rule.* On the assumption that gas mixtures could be considered as perfect solutions, Lewis and Randall[14] proposed: The fugacity of a gas in a mixture is equal to the product of the fugacity of the pure gas existing at the temperature and under the total pressure of the mixture multiplied by the mole fraction of that gas in the mixture. Gillespie[5] has shown that this rule applies only when Amagat's law holds for the gas mixture. Hence the Lewis and Randall rule leads to the equation of state (2) for gas mixtures.

Thus the first two laws result in an equation of state of the type (1) for a mixture of gases, while the latter two give an equation of the type (2). Either Dalton's or Amagat's law can be used wtihout the aid of an equation of state provided that compressibility data on the pure gases are available.

It has been generally accepted[15] that Amagat's law gives more satisfactory results than Dalton's law for the permanent gases. Lurie and Gillespie[12] have shown that the Lewis and Randall rule gives more satisfactory results than the Gibbs-Dalton law when applied to the calculation of the "equilibrium pressure" of ammonia in mixtures of nitrogen and ammonia. Keyes and Burks[16] found that Amagat's law is a better approximation than Dalton's law of "partial pressures" in terms of weight fraction (rather than mole fractions) for mixtures of nitrogen and methane. Masson and Dolley[17] found that Amagat's law gave a better representation of their measurements on argon-oxygen mixtures than Dalton's law although the reverse was the case for argon-ethylene and oxygen-ethylene mixtures. All of these comparisons show that Dalton's and Amagat's laws each give an increasingly good representation of the experimental data as the pressure is diminished, but that they may lead to large errors at moderately high pressures especially when one of the gases is much more compressible than the other.

(b) *The van der Waals Equation of State.*

There have been many investigations concerned with the repre-

sentation of the pressures of gas mixtures by use of van der Waals' equation of state:[18]

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{3}$$

in which R is the ideal gas constant, a and b constants for each gas, and v the volume of a unit mass, say one mole, of the gas.

General considerations indicate that the equation of state of a mixture of gases which do not react chemically should be of the same form as that for the pure component gases and the same conclusion is reached by use of statistical mechanics.[19] Thus from the standpoint of empirically representing the compressibility data, it should be possible to select values of a and b which give as satisfactory a result for a mixture of gases as for the pure constituent gases. Since the time of van der Waals it has further been the expectation that the values of the parameters for any given gas mixture could be calculated from the constants of the pure component gases and the composition of the mixture. General considerations and statistical mechanics again concur in indicating that each of the constants a and b should be combined with the composition in the most general quadratic manner. Thus for the b constant we may write:

$$b_x = b_1 x_1^2 + 2b_{12} x_1 x_2 + b_2 x_2^2 \tag{4}$$

In this relation b_1 and b_2 are the values of the b constant for the pure Gases 1 and 2, b_x the value of this constant for a binary mixture of these gases the composition of which is expressed in terms of the mole fractions x_1 and x_2, and b_{12} a so-called "interaction constant" which arises from the interaction of unlike molecules. Thus when applying equation (3) to the gas mixture we can replace b by b_x and a by a_x, using for v the volume of an average mole of mixture.

Several methods for evaluating the interaction constants have been suggested, the two simplest of which are that they may be taken as the arithmetic, or as the geometric mean of the corresponding constants for the pure gases. Thus for the b constants we may write:

$$b_{12} = \tfrac{1}{2}(b_1 + b_2) \tag{5}$$

or:

$$b_{12} = (b_1 b_2)^{1/2} \tag{6}$$

When these are substituted into (4) there results for b_x:

$$b_x = b_1 x_1 + b_2 x_2 \tag{7}$$

or:

$$b_x^{1/2} = b_1^{1/2}x_1 + b_2^{1/2}x_2 \tag{8}$$

The first of these methods for computing b_x, equation (7), will be called linear combination of constants and was used to some extent by van der Waals and by Berthelot[20] for the b constant; the latter method, equation (8), will be called linear combination of $b^{1/2}$ or linear square root combination and was used by Galitzine[21] and by Berthelot[20] for the cohesive constant a.

On the assumption that the molecules are elastic spheres and that the distance of closest approach of the centers of any two molecules is the sum of the radii of the two molecules in question, Lorentz[22] derived for the b_{12} interaction constant the value:

$$b_{12}^{1/3} = \tfrac{1}{2}(b_1^{1/3} + b_2^{1/3}) \tag{9}$$

Thus:

$$b_x = b_1x_1^2 + \tfrac{1}{4}(b_1^{1/3} + b_2^{1/3})^3x_1x_2 + b_2x_2^2 \tag{10}$$

We shall call this the Lorentz method of combination. It has been quite generally employed[23] for b_x. It is questionable however if the b constant should be linked too intimately with the distance of closest approach of the molecules. On the basis of Phillips'[24] view, any kind of interaction between the molecules of a gas would give rise to a b term; that is, the pressure of the gas would be increased by any type of interaction, regardless of whether the interaction is due to attractive or repulsive forces, regardless of the law of the forces and further, independent of the size of the molecules, which may be infinitesimal.

Because of the failure of van der Waals' equation to give even an approximate representation of the compressibility of pure gases over a wide range of temperature and density, it has never been applied to compressibility data on gas mixtures except[23] at relatively low pressures.

(c) *The Keyes Equation of State.*

The first quantitative treatment of gas mixtures at relatively high pressures was by means of the Keyes equation of state:[4]

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{11}$$

in which R is the gas constant and α, β, A and l constants for each gas. Lurie and Gillespie[12] applied this equation to the calculation

of the equilibrium pressures of ammonia in a mixture of ammonia and nitrogen to 60 atmospheres at 45° C. They used linear combination for each of the constants R, α, β, $A^{1/2}$ and l as suggested by Keyes and stated that the computed values agreed with the experimental data possibly to within the experimental data. Keyes and Burks[16] measured the compressibility of mixtures of nitrogen and methane to about 300 atmospheres and from 0 to 200° C. They determined the values of the four adjustable constants of (11) for each of the mixtures investigated, thus definitely proving that the compressibility of the mixtures and of the pure gases can be represented by the same type of equation of state. They further found that each of the constants as determined from the data on the mixtures could be satisfactorily calculated from the values of the constants for the pure gases and the composition by the method mentioned above.

(d) *The Beattie-Bridgeman Equation of State.*

One of the authors[25] has applied to gas mixtures the Beattie-Bridgeman[26] equation of state:

$$p = \frac{RT(1-\varepsilon)}{v^2}[v + B] - \frac{A}{v^2} \tag{12}$$

$$A = A_0(1 - a/v)$$

$$B = B_0(1 - b/v)$$

$$\varepsilon = c/vT^3$$

in which R is the ideal gas constant and A_0, a, B_0, b and c are constants for each gas. The pressures of the nitrogen-methane mixtures as measured by Keyes and Burks are well represented when the values of the parameters for the mixtures are computed by linear combination of each of the constants R, A_0,$^{1/2}$ a, B_0, b and c. The values of the constants of the pure gases used were those determined from the data of Smith and Taylor[27] on nitrogen and of Keyes and Burks[28] on methane; the former having used the same apparatus for the compressibility measurements on nitrogen as the latter used for methane and the mixtures.

(e) *Other Methods.*

Several other methods of attack on the problem of the equation of state of gas mixtures have been made. Thus Lennard-Jones and

Cook[29] have shown that the second virial coefficient should be quadratically combined in the manner of equation (4) but that the interaction constant is not related in any simple manner to the coefficients for the pure gases. A relation for the interaction constant is given in terms of the force constants appearing in the equation representing the attractive and repulsive forces between molecules of unlike type. The relations obtained are too involved for general use.

Deming and Shupe,[30] extending a method suggested by Kleeman,[31] have calculated the pressures of the binary mixtures of nitrogen and methane investigated by Keyes and Burks by combining each of the coefficients in the general virial equation:

$$p = \frac{A_1}{v} + \frac{A_2}{v^2} + \frac{A_3}{v^3} + \frac{A_4}{v^4} + \cdots \tag{13}$$

according to the method:

$$A_{mx} = [\Sigma x_i \varepsilon_{mi} (\varepsilon_{mi} A_{mi})^{1/m}]^m \tag{14}$$

where A_{mx} is the mth virial coefficient of the mixture; A_{m1}, A_{m2}, $\cdots$ the mth coefficients of the pure Gases 1, 2, $\cdots$; x_1, x_2, $\cdots$ the mole fractions of the gases in the mixture; and $\varepsilon_{mi} = +1$ or -1, whichever is required to make the product $\varepsilon_{mi} A_{mi}$ positive. The summation extends over all the gases in the mixture. The method is applicable when the values of the virial coefficients for the pure components have been determined at a single temperature only. Deming and Shupe found that this method does not give quite so good an overall representation of the nitrogen-methane data as the Beattie-Bridgeman equation of state for mixtures although in the low temperature high pressure corner of the table the representation is somewhat better.

Van Lerberghe[32] has noticed that the generalized equation of state for a gas mixture:

$$p = f(T, V, n_1, n_2, \cdots) \tag{15}$$

in which V is the total volume and n_1, n_2, $\cdots$ the mole numbers of the Gases 1, 2, $\cdots$ in the mixture, can be developed into a Maclaurin series. This gives for a binary mixture the result:

$$p = p_1 + p_2 + \frac{n_1 n_2}{V^2} \omega_{12} \tag{16}$$

in which p_1 and p_2 are the pressures exerted by the Gases 1 and 2

respectively at the temperature T of the mixture and the molal concentrations n_1/V and n_2/V. The quantity ω_{12} is a function of the temperature and must be determined for each pair of substances. This relation represents the methane-nitrogen data well but it should be noted that in addition to data on the pure gases it is necessary to have available information concerning ω_{12} at each temperature, or the empirical temperature function for ω_{12} for each pair of gases. Thus new constants which cannot be calculated from those of the pure gases are introduced. This limits the usefulness of the method.

3. Previous Work on the Methods of Combination of the Constants.

Three methods of combining constants have been mentioned: linear, equation (7); linear square root, equation (8); and Lorentz, equation (10). For any given values of the constants for the pure gases, linear combination leads to the greatest value of the corresponding parameter for the mixture, linear square root to the smallest, and Lorentz combination to an intermediate value.

When an equation of state constant has the dimensions of volume, linear combination for the corresponding parameter for the mixture gives the simplest resulting equation; when the constant has the dimensions of volume squared, linear square root combination gives the simplest result; while the Lorentz method does not lead to simple equations in any case. In the first two cases mentioned the constants can be combined with the mole-numbers of the component gases instead of the mole fractions. Many of the uses to which an equation of state for gas mixtures is put require differentiation with respect to mole-numbers, and the resulting equations are simpler when mole-numbers can be used in the combination equations (7) or (8).

There have been three methods proposed for determining the interaction constant b_{12} and two for a_{12}, the Lorentz derivation not applying to this latter case. It is for experiment to determine:

(1) Which of these methods of combining constants gives the most satisfactory representation of the experimental compressibility data on gas mixtures.

(2) Which of these methods, if any, leads to an equation of state for gas mixtures that, when used to integrate the general equations for the thermodynamic properties of gas mixtures, gives relations which represent these properties satisfactorily.

(3) Which of the three methods: combination of the constants in

an equation of state, Dalton's law, Amagat's law gives the best results; and how much better is the preferred method.

The present paper deals with the first and last of these statements. There have been several investigations that have treated the question of what is the best method of combination for a given constant. We are concerned mainly with the a and b constants of van der Waals' equations or the corresponding constants A and β of the Keyes or A_0 and B_0 of the Beattie-Bridgeman equation. The methods of combination used for the higher order constants in the latter two equations of state are not so important since in general these constants do not have so great an effect on the calculation of the pressure.

In the evaluation of some of the thermodynamic properties of gas mixtures, the cohesive constant a has a relatively greater effect than any of the others. Eucken and Bresler[33] from their own measurements and those of Pollitzer and Strebel[34] on the effect of an indifferent gas on the vapor pressure of liquids calculated values of the interaction constant a_{12} by the use of certain expressions for the equilibrium pressures and the van der Waals equation of state. The b_{12} interaction constant was calculated by the Lorentz method, but it was remarked that the method of combination used for b did not greatly influence the result since the b constant does not enter markedly into the calculation. They found that the best representation of the interaction constant was given by linear square root combination for a.

Gillespie[35] investigated the limiting value of the expansion of a gas in a gas mixture as the pressure approaches zero at constant temperature and composition. The general relation for the intercept is:

$$\lim_{p \to 0} (\bar{v}_1 - v_1) = x_2^2 \left[\frac{A_{01} - 2A_{012} + A_{02}}{RT} - (B_{01} - 2B_{012} + B_{02}) \right] \quad (17)$$

where $\bar{v}_1$ is the partial molal volume of the Gas 1 in the mixture and v_1 the molal volume of Gas 1 in the pure state at the temperature and under the pressure of the mixture. The same expression results whether the van der Waals, Keyes, or Beattie-Bridgeman equation of state is used provided that in the latter two equations all of the higher order constants are combined according to the linear method. Since Gillespie actually used the values of the constants of the latter equation of state in his computations, it is written here in terms of these constants.

Twelve binary mixtures for which compressibility data existed in

the literature were investigated by Gillespie; five for argon-ethylene mixtures, three for oxygen-ethylene, one for hydrogen-nitrogen, and three for nitrogen-methane. He found that the value of the intercept obtained by extrapolation of the values of $\bar{v}_1 - v_1$ determined from the experimental data to zero pressures is not zero as had been assumed by some writers but has in all of the cases studied a finite positive value.

When linear combination, equation (7), is used for B_0, the quantity $(B_{01} - 2\,B_{012} + B_{02})$ is zero [by equation (5)] and when either linear square root or Lorentz combination, equations (8) or (10) respectively, are used this quantity is positive since twice the interaction constant B_{012} determined by (6) or (9) is less than the sum of the constants for the pure gases. Thus linear combination for A_0 is excluded since in this case the contribution from the A_0 constant to the value of the intercept would be zero and the calculated intercept would be zero or negative. Moreover Gillespie showed that when linear square root combination was used for A_{0x} and either linear or Lorentz combination for B_{0x}, a good representation of the experimental intercepts was obtained. The argon-ethylene data pointed to the Lorentz method for B_{0x}, the oxygen-ethylene to the linear method, while the other two binary combinations did not strongly support either method but perhaps favored the linear method slightly. In no case was it impossible to exclude either method since the effect of B_0 on the calculation was smaller than that of the A_0 constant. On the other hand the linear square root combination for B_{0x} seems to be excluded since in all cases in which any doubt existed the values of intercepts obtained by extrapolation of the plots lay rather between those calculated by linear and Lorentz combination for B_0, whereas linear square root combination for B_{0x} would cause the calculated intercept to fall below the Lorentz value.

This investigation definitely indicates the linear square root combination for A_0 and either linear or Lorentz combination for B_0 with the linear method slightly favored.

4. The Equation of State for Mixtures used in the Present Comparisons.

The virial form of the equation of state (12) when written for a gas mixture is:

$$p = \frac{R_n T}{V} + \frac{\beta_n}{V^2} + \frac{\gamma_n}{V^3} + \frac{\delta_n}{V^4} \qquad (18)$$

$$\beta_n = R_n T B_{0n} - A_{0n} - R_n c_n / T^2$$

$$\gamma_n = - R_n T B_{0n} b_n + A_{0n} a_n - R_n B_{0n} c_n / T^2$$

$$\delta_n = R_n B_{0n} b_n c_n / T^2$$

where R_n, A_{0n}, a_n, B_{0n}, b_n and c_n are the values of the parameters for a mixture consisting of n_1, n_2, . . . moles of the Gases 1, 2, . . . respectively and V is the volume of Σn_i moles of the mixture. Any equation may be used for computing the values of the parameters from the constants of the pure gases and the composition; but a method that gave good results in the calculation of the pressures of nitrogen-methane mixtures[25] and of the expansion[35] of gases on mixing at low pressures is linear combination for each of the constants R, $A_0^{1/2}$, a, B_0, b and c, namely:

$$\begin{aligned}
R_n &= n_1 R + n_2 R + \cdots &&= \Sigma(n_i)R && (19)\\
A_{0n} &= (n_1 A_{01}^{1/2} + n_2 A_{02}^{1/2} + \cdots)^2 &&= (\Sigma n_i A_{0i}^{1/2})^2\\
a_n &= n_1 a_1 + n_2 a_2 + \cdots &&= \Sigma(n_i a_i)\\
B_{0n} &= n_1 B_{01} + n_2 B_{02} + \cdots &&= \Sigma(n_i B_{0i})\\
b_n &= n_1 b_1 + n_2 b_2 + \cdots &&= \Sigma(n_i b_i)\\
c_n &= n_1 c_1 + n_2 c_2 + \cdots &&= \Sigma(n_i c_i)
\end{aligned}$$

In these relations $n_1, n_2, \cdots$ may represent: (1) the number of moles of the component gases, in which case the volume V used in (18) is the total volume of Σn_i moles; (2) the mole fraction of the component gases, the volume v being the volume of an average mole of mixture, that is $V/\Sigma n_i$; (3) the weight fractions of the component gases, the volume v referring to one gram of mixture. In the latter case R has a different value for each gas and $R_n = \Sigma(n_i R_i)$.

The method of combination (19) not only gives a satisfactory representation of the experimental data in the several cases in which it has been used, but leads to relatively simple equations for the thermodynamic properties of gas mixtures. Provisionally, we may consider that the method of combination is settled for all of the constants except for B_0 which, in addition to the method shown in (19), may also be combined either by the Lorentz or the linear square root method. In the former case all of the equations of (19) remain the same except that for B_{0n} which becomes:

$$B_{0x} = x_1^2 B_{01} + \tfrac{1}{4} x_1 x_2 (B_{01}^{1/3} + B_{02}^{1/3})^3 + x_2^2 B_{02} \qquad (20)$$

and in the latter case it is necessary to replace the relation for B_{0n} of (19) by:

$$B_{0x} = (\Sigma x_i B_{0i}^{1/2})^2 \tag{21}$$

In (20) and (21) only the mole fraction may be used since the quantity B_0 has the dimensions of volume. For the calculation of the pressures of a gaseous mixture, the use of either of these methods of combination does not introduce serious difficulties; but either expression leads to rather involved relations for some of the thermodynamic properties of gas mixtures, especially those requiring differentiation with respect to the composition.

5. The Experimental Data.

The earlier work[36] on the compressibility of gaseous mixtures was rather fragmentary. Recently, however, there have been several investigations that extend to moderately high pressures:

1. Kuenen, Verschoyle and van Urk[37] measured the compressibility of two mixtures of oxygen and nitrogen. These data are not treated in the present paper since they are for the most part in the critical region and also because the values of the equation of state constants for oxygen and nitrogen are so similar that the comparison would have very little bearing on the mixture equation of state.

2. Masson and Dolley[17] measured the compressibility of five mixtures of argon with ethylene, three mixtures of oxygen with ethylene, one of argon with oxygen, and of the three pure gases at 24.95° C. and to 125 atmospheres. The gas compositions were expressed as percentages by volume of the separate components each taken at 24.95° C. and 1 atmosphere. The volumes of each mixture were given in terms of the sum of the volumes of the component gases each measured at 24.95° C. and 1 atmosphere.

3. Verschoyle[38] determined the compressibility of three mixtures of hydrogen and nitrogen and of the two pure gases at 0° and 20° C. to 200 atmospheres. The meaning of the term "percentage composition" was not stated, so that it was assumed that this expression denoted percentages by volume of the separate components each taken at 20° C. For each mixture the unit of volume was the volume of that mixture at 0° C. and 1 atmosphere.

4. Keyes and Burks[16, 28] studied the compressibility of three mixtures of nitrogen and methane and of methane from 0° to 200° C. and to about 300 atmospheres. Smith and Taylor[27] using the same apparatus had previously studied the compressibility of pure nitrogen.

The composition of the mixtures were given in percentages by weight, and volumes in ccm. per gram.

5. Bartlett, Cupples and Tremearne[39] determined the compressibility of one mixture of hydrogen and nitrogen and of the pure gases from 0° to 400° C. and to 1000 atmospheres. These data are not treated in the present paper.

6. Gibby, Tanner and Masson[40] studied the compressibility of one mixture of helium and hydrogen and of the pure gases from 25 to 175° C. and of several mixtures at 25° C. The original data are not given, but they list the parameters a and b of the relation:

$$pv = a + bp$$

for each isotherm of each mixture. The curve obtained by plotting the values of b against the composition of the corresponding mixture for 25° C. exhibits a maximum of about 80% hydrogen. Thus some mixtures of hydrogen and helium are less compressible than either of the pure gases.

7. Scott[41] measured the compressibility of three mixtures of hydrogen and carbon monoxide and of the pure gases at 25° C. and to 170 atmospheres. The meaning of "percentage composition" is not given but it is stated that the compositions were determined by chemical analyses. This may mean that the compositions are percentages by volume at some low pressure or true molal percentages. In our treatment of these data it was assumed that compositions were expressed in mole percent, the difference between the two methods of giving compositions being probably within the experimental error of the measurements. Volumes were given in terms of the volumes of the mixtures at 25° C. and 1 atmosphere each of which was assumed to have the value 1.09155 under these conditions.

In all of the measurements mentioned above temperatures were expressed in degrees centigrade and it is assumed that pressures were in normal atmospheres.

In Table I is given a résumé of the methods of expressing compositions used by the four groups of investigators whose data are treated in the present paper, together with the corresponding mole fractions. The values of the molal volumes of the pure gases used for the data of Masson and Dolley and of Verschoyle were computed from the equation of state.

6. Treatment of the Experimental Data.

The values of the constants of the Beattie-Bridgeman equation of state for several gases have been published[26,35] in units of atmospheres, liters per mole and degrees Kelvin. In Table II are given a résumé of the volume units in which the data of the four groups of observers are expressed and the conversion factor by which the density in moles per liter must be multiplied to reduce it to the units in which the data are given.

In order to calculate the value of the conversion factor for Masson and Dolley's measurements it is required to know the molal volumes of the pure gases at 24.95° C. and 1 atmosphere, and these values were computed from the equation of state for these gases.

For the measurements of Verschoyle and of Scott it is necessary to know the molal volumes of the mixtures at 20° C and 1 atmosphere. and at 25° C. and 1 atmosphere respectively. These values were computed from the equation of state for mixtures. It is evident that this computed value depends on the method of combination of constants used. Hence in each case one factor was calculated using the linear method of equation (19), and one factor using the method of (19) for all constants except B_{0x} for which the Lorentz method (20) was used. The first factor was employed whenever linear combination for B_{0x} was used as in Table IV and the second when Lorentz combination was used, Table V.

The measurements of Keyes and Burks were expressed in volume units of ccm. per gram, and the calculations were made in the same units.

In Table III are given the values of the equation of state constants for the pure gases and of the parameters for the mixtures calculated according to the relations (19). There is also given in each case the value of B_{0x} obtained by using Lorentz combination, equation (20). For the data of Keyes and Burks the weight fractions and the values of the constants in units of ccm. per gram were substituted into (19). In the Lorentz combination of B_0 for the latter data however the calculation was carried out using mole fractions and the values of B_0 for the pure gases in ccm. per mole. The value of B_{0x} so obtained was divided by the average molecular weight of the mixture given in Table I to obtain the value of B_{0w} which can be used when volumes are in ccm. per gram.

In Table IV are given the values of the virial coefficients β_n, γ_n and δ_n of equation (18) for each of the pure gases and mixtures at

TABLE I.

CALCULATION OF THE COMPOSITIONS IN MOLE FRACTIONS.

1. *Data of Masson and Dolley.*

Compositions expressed as percentages by volume of the separate constituents each taken at 24.95°C. and 1 atm.

Gas	Argon	Oxygen	Ethylene
Molal volume at 24.95°, 1 atm. (liters)	24.4448	24.4440	24.3214

Volume percent		Mole fraction	
A	C_2H_4	A	C_2H_4
75.26	24.74	0.7517	0.2483
50.05	49.95	.4992	.5008
40.14	59.86	.4002	.5998
29.28	70.72	.2918	.7082
9.94	90.06	.0989	.9011

Volume percent		Mole fraction	
O_2	C_2H_4	O_2	C_2H_4
74.73	25.27	0.7463	0.2537
50.09	49.91	.4996	.5004
40.16	59.84	.4004	.5996

Volume percent		Mole fraction	
A	O_2	A	O_2
49.99	50.01	0.4999	0.5001

2. *Data of Verschoyle.*

Compositions expressed as percentages by volume of the separate constituents each taken at 20°C. and 1 atm.

Gas	Hydrogen	Nitrogen
Molal volume at 20°, 1 atm. (liters)	24.0670	24.0472

Volume percent		Mole fraction	
H_2	N_2	H_2	N_2
75.00	25.00	0.7498	0.2502
50.00	50.00	.4998	.5002
25.00	75.00	.2498	.7502

TABLE I—Concluded.

3. *Data of Keyes and Burks.*

Compositions expressed as percentages by weight.

Gas		Nitrogen	Methane	
Molecular Weight		28.016	16.0308	

Weight percent		Mole fraction		Average mol. wt.
N_2	CH_4	N_2	CH_4	
69.556	30.444	0.5666	0.4334	22.8216
31.014	68.986	.2046	.7954	18.4831
29.69	70.31	.1946	.8054	18.3632

4. *Data of Scott.*

Compositions expressed as molal percentages (determined by chemical analyses).

Mole percent		Mole fraction	
H_2	CO	H_2	CO
66.3	33.7	0.663	0.337
51.7	48.3	.517	.483
33.1	66.9	.331	.669

each of the temperatures for which compressibility data exist. The values of the parameters for the mixtures are those obtained by use of the method of combination (19) and appear in Table III. The virial coefficients are given first in units of atmospheres, liters per mole and degrees Kelvin and then in the volume units of the data. The conversion was made by dividing RT, β_n, γ_n and δ_n by the appropriate factor given in Table II raised to the first, second, third and fourth powers respectively.

In Table V the values of the virial coefficients are given when the method of combination (19) is used for all constants except B_0 which is combined by the Lorentz method (20). The conversion factors used in this case for the data of Verschoyle and Scott are those listed in Table II under the heading "Lorentz B_{0x}."

The virial coefficients were not computed for the data of Keyes and Burks since their measurements were made by the isometric method. The calculated values were computed accordingly, as described in an earlier paper.[25]

It is to be noted that there are no measurements of the compressibility of carbon monoxide that extend over a sufficiently wide temperature and pressure range to permit the determination of the equation of state constants for this gas. Computations[42] of the weight of a normal liter of carbon monoxide by use of the constants for nitrogen have confirmed the conclusion drawn from Langmuir's[43] theory of isosters that the constants for carbon monoxide should not differ greatly from those for nitrogen. Accordingly, in the present comparison the constants for nitrogen were used for carbon monoxide and this procedure is justified by the fact that to 170 atmospheres the deviation between the calculated and observed pressures for carbon monoxide are of the same order of magnitude as those for hydrogen (see Figure 21).

A value of the pressure was calculated from the virial coefficients given in Table IV, and one from the values given in Table V for each observed point of Masson and Dolley, Verschoyle, and Scott. Corresponding computations were made with the aid of the values given in Table III for the results of Keyes and Burks. The percentage deviations of the calculated from the observed pressures:

$$\% = 100 \frac{\text{obs. pressure} - \text{calcd. pressure}}{\text{obs. pressure}}$$

were plotted against the observed pressures for each case. The

plots are given in Figures 1 to 24. Figures 1, 10, 14 and 21 exhibit the results for the pure gases. For each mixture there are two curves: one, marked "Lin," representing the deviations when the method of combination (19) is used for all constants; and, the other, marked "Lor," giving the deviation when the relations (19) are used for all of the constants except B_0 which is combined according to the Lorentz method (20). On each mixture plot for the data of Masson and Dolley, Verschoyle, and Scott there also appears a curve, marked "Sum," the ordinate of which at a given pressure is the sum $(x_1\%_1 + x_2\%_2)$ where x_1 and x_2 refer to the mole fraction of the Gases 1 and 2 in the mixture, and $\%_1$ and $\%_2$ to the percentage deviations (from Figure 1, 10, 14 or 21) for the pure gases at that pressure.

Although in some cases there were slight irregularities, smooth curves were drawn except for the data of Verschoyle. No curves are given for the argon-oxygen mixture since the three curves "Lin," "Lor," and "Sum" practically coincide when plotted on the same scale as that used for the other figures.

TABLE II.

Calculation of the Volume Conversion Factors.

$$\text{Conversion factor} = \frac{\text{Volume in liters per mole.}}{\text{Volume in units of experimental data.}}$$

1. *Data of Masson and Dolley.*

$$\text{Volume (M and D)} = \frac{\text{Volume of mixture at 24.95° C. and } p \text{ atm.}}{\text{Sum of volumes of separate constituents each taken at 24.95° C. and 1 atm.}}$$

Factor = $\Sigma(x_i V_i)$; V_1 = molal volume in liters of Gas 1 at 24.95° C. and 1 atm.

Mole fraction A	Mole fraction C_2H_4	Factor	Mole fraction O_2	Mole fraction C_2H_4	Factor	Mole fraction A	Mole fraction O_2	Factor
1.0000	0.0000	24.4448	1.0000	0.0000	24.4440	1.0000	0.0000	24.4448
0.7517	0.2483	24.4142	0.7463	0.2537	24.4129	0.4999	0.5001	24.4444
0.4992	0.5008	24.3830	0.4996	0.5004	24.3827	0.0000	1.0000	24.4440
0.4002	0.5998	24.3708	0.4004	0.5996	24.3705			
0.2918	0.7082	24.3574	0.0000	1.0000	24.3214			
0.0989	0.9011	24.3336						
0.0000	1.0000	24.3214						

TABLE II.—Concluded.

2. *Data of Verschoyle.*

$$\text{Volume (Verschoyle)} = \frac{\text{Volume of mixture at } t^\circ \text{ C. and } p \text{ atm.}}{\text{Volume of mixture at } 0^\circ \text{ C. and 1 atm.}}$$

Factor = molal volume in liters of mixture at 0° C. and 1 atm.

Mole fraction H_2	Mole fraction N_2	Factor Linear B_{0x}	Factor Lorentz B_{0x}
1.0000	0.0000	22.425204	
0.7498	0.2502	22.423559	22.422760
0.4998	0.5002	22.419065	22.418000
0.2498	0.7502	22.411722	22.410924
0.0000	1.0000	22.401534	

3. *Data of Keyes and Burks.*

Volume (K and B) = Specific volume in cubic centimeters per gram. Calculations carried out in same volume units.

4. *Data of Scott.*

$$\text{Volume (Scott)} = \frac{\text{Volume of mixture at } 25^\circ \text{ C. and } p \text{ atm.}}{\text{Volume of mixture at } 25^\circ \text{ C. and 1 atm.}} \times 1.09155.$$

$$\text{Factor} = \frac{V}{1.09155};\ \text{V = molal volume in liters of mixture at } 25^\circ \text{ C. and 1 atm.}$$

Mole fraction H_2	Mole fraction CO	V (Linear B_{0x})	Factor (Linear B_{0x})	V (Lorentz B_0)	Factor (Lorentz B_0)
1.000	0.000	24.477445	22.424484		
0.663	0.337	24.475739	22.422921	24.474786	22.422048
0.517	0.483	24.473527	22.420894	24.472462	22.419918
0.331	0.669	24.469419	22.417131	24.468475	22.416266
0.000	1.000	24.458534	22.407159		

TABLE III.

Values of the Parameters in the Beattie-Bridgeman Equation of State.

Equation of state given in equation (12); virial form in equation (18).

Method of combination of constants given in equations (19); Lorentz method for B_{0x} in (20).

Units: normal atmospheres, liters per mole, degrees Kelvin (T°K = t° C + 273.13); except for Keyes and Burks' data for which volumes are in ccm. per gram.

1. *Data of Masson and Dolley.*

Mole fraction		$\Sigma(x_i)R$	$(\Sigma x_i A_{0i}^{1/2})^2$	$\Sigma(x_i a_i)$	$\Sigma(x_i B_{0i})$	$\Sigma(x_i b_i)$	$\Sigma(x_i c_i) \times 10^{-4}$	Lorentz B_{0x}
A	C_2H_4							
1.0000	0.0000	0.08206	1.2907	0.02328	0.03931	0.0	5.99	
0.7517	0.2483	0.08206	2.16050	0.029825	0.059733	0.008931	10.134	0.056910
0.4992	0.5008	0.08206	3.27350	0.036481	0.080501	0.018014	14.348	0.076720
0.4002	0.5998	0.08206	3.77276	0.039091	0.088644	0.021575	16.001	0.085014
0.2918	0.7082	0.08206	4.36006	0.041948	0.097559	0.025474	17.810	0.094435
0.0989	0.9011	0.08206	5.51018	0.047033	0.113425	0.032413	21.029	0.112078
0.0000	1.0000	0.08206	6.1520	0.04964	0.12156	0.03597	22.68	
O_2	C_2H_4							
1.0000	0.0000	0.08206	1.4911	0.02562	0.04624	0.004208	4.80	
0.7463	0.2537	0.08206	2.37335	0.031714	0.065349	0.012266	9.336	0.063090
0.4996	0.5004	0.08206	3.42701	0.037640	0.083930	0.020102	13.747	0.080948
0.4004	0.5996	0.08206	3.90510	0.040022	0.091402	0.023252	15.521	0.088538
A	O_2							
0.4999	0.5001	0.08206	1.38911	0.024450	0.042776	0.002104	5.395	0.042729

TABLE III.—Concluded.

2. *Data of Verschoyle.*

Mole fraction H_2	Mole fraction N_2	$(\Sigma x_i)R$	$(\Sigma x_i A_{0i}^{1/2})^2$	$\Sigma(x_i a_i)$	$\Sigma(x_i B_{0i})$	$\Sigma(x_i b_i)$	$\Sigma(x_i c_i)\times 10^{-4}$	Lorentz B_{0x}
1.0000	0.0000	0.08206	0.1975	−0.00506	0.02096	−0.04359	0.0504	
0.7498	0.2502	0.08206	0.38854	+0.002754	0.028341	−0.034413	1.08863	0.027542
0.4998	0.5002	0.08206	0.64338	+0.010561	0.035716	−0.025243	2.12603	0.034651
0.2498	0.7502	0.08206	0.96214	+0.018369	0.043091	−0.016073	3.16343	0.042293
0.0000	1.0000	0.08206	1.3445	+0.02617	0.05046	−0.00691	4.20	

3. *Data of Keyes and Burks.*

Weight fraction N_2	Weight fraction CH_4	$\Sigma(w_i R_i)$	$(\Sigma w_i A_{0i}^{1/2})^2$	$\Sigma(w_i a_i)$	$\Sigma(w_i B_{0i})$	$\Sigma(w_i b_i)$	$\Sigma(w_i c_i)\times 10^{-6}$	Lorentz B_{0w}
1.0000	0.0000	2.92904	1457.5	0.6382	1.5398	−0.5740	2.00	
0.69556	0.30444	3.59572	3048.2	0.7961	2.1321	−0.7006	3.827	2.1262
0.31014	0.68986	4.43974	5894.4	0.9961	2.8819	−0.8610	6.139	2.8770
0.2969	0.7031	4.46873	6008.7	1.0030	2.9076	−0.8665	6.219	2.9029
0.0000	1.0000	5.11890	8860.0	1.1570	3.4852	−0.9900	8.00	

4. *Data of Scott.*

Mole fraction H_2	Mole fraction CO	$\Sigma(x_i)R$	$(\Sigma x_i A_{0i}^{1/2})^2$	$\Sigma(x_i a_i)$	$\Sigma(x_i B_{0i})$	$\Sigma(x_i b_i)$	$\Sigma(x_i c_i)\times 10^{-4}$	Lorentz B_{0x}
1.000	0.000	0.08206	0.1975	−0.00506	0.02096	−0.04359	0.0504	
0.663	0.337	0.08206	0.46978	+0.005465	0.030902	−0.031229	1.44882	0.029950
0.517	0.483	0.08206	0.62380	+0.010024	0.035209	−0.025874	2.05466	0.034145
0.331	0.669	0.08206	0.85160	+0.015833	0.040696	−0.019051	2.82648	0.039752
0.000	1.000	0.08206	1.3445	+0.02617	0.05046	−0.00691	4.20	

TABLE IV.

VALUES OF THE VIRIAL COEFFICIENTS.

Linear combination of R, $A_0^{1/2}$, a, B_0, b and c.

Virial coefficients calculated by use of the relations (18) from the values given in Table III.

"Normal units" are normal atmospheres, liters per mole, degrees Kelvin.

"Units of data" are normal atmospheres, volume units in which experimental data are expressed (see Table II), degrees Kelvin.

1. *Data of Masson and Dolley.*

$t = 24.95°$ C.

Mole fraction		Virial coefficients in normal units				Virial coefficients in units of data			
A	C_2H_4	RT	β_n	$\gamma_n \times 10^2$	$\delta_n \times 10^4$	RT	$\beta_n \times 10^3$	$\gamma_n \times 10^6$	$\delta_n \times 10^9$
1.0000	0.0000	24.460445	−0.3844812	2.787282	0.0	1.000640	−0.64343	1.9082	0.0
0.7517	0.2483	24.460445	−0.7929980	4.579723	0.49930	1.001894	−1.33041	3.1471	0.141
0.4992	0.5008	24.460445	−1.4369223	7.328196	1.92162	1.003176	−2.41690	5.0552	0.544
0.4002	0.5998	24.460445	−1.7522674	8.760077	2.82627	1.003678	−2.95026	6.0520	0.801
0.2918	0.7082	24.460445	−2.1382098	10.605914	4.08784	1.004231	−3.60403	7.3393	1.161
0.0989	0.9011	24.460445	−2.9299698	14.720391	7.14023	1.005213	−4.94824	10.2165	2.037
0.0000	1.0000	24.460445	−3.3880521	17.296925	9.15883	1.005717	−5.72760	12.0227	2.617
O_2	C_2H_4								
1.0000	0.0000	24.460445	−0.4043800	3.139266	0.08626	1.000673	−0.67678	2.1494	0.024
0.7463	0.2537	24.460445	−0.8611081	5.002701	0.69114	1.001948	−1.44484	3.4383	0.195
0.4996	0.5004	24.460445	−1.5010069	7.706803	2.14205	1.003189	−2.52475	5.3165	0.606
0.4004	0.5996	24.460445	−1.8127124	9.120253	3.04650	1.003691	−3.05211	6.3011	0.864
A	O_2								
0.4999	0.5001	24.460445	−0.3926161	2.963092	0.04484	1.000656	−0.65707	2.0286	0.013

TABLE IV.—Concluded.

2. *Data of Verschoyle.*

$t = 20°$ C.

Mole fraction		Virial coefficients in normal units				Virial coefficients in units of data			
H_2	N_2	RT	β_n	$\gamma_n \times 10^2$	$\delta_n \times 10^4$	RT	$\beta_n \times 10^3$	$\gamma_n \times 10^6$	$\delta_n \times 10^9$
1.0000	0.0000	24.054248	0.3061957	2.096764	−0.00440	1.072643	0.60887	1.8593	−0.002
0.7498	0.2502	24.054248	0.2827848	2.423547	−0.10140	1.072722	0.56240	2.1495	−0.040
0.4998	0.5002	24.054248	0.1954376	2.775637	−0.18306	1.072937	0.38884	2.4633	−0.072
0.2498	0.7502	24.054248	0.0441703	3.303173	−0.20924	1.073289	0.08794	2.9343	−0.083
0.0000	1.0000	24.054248	−0.1708334	4.154878	−0.13986	1.073777	−0.34042	3.6959	−0.056

$t = 0°$ C.

H_2	N_2								
1.0000	0.0000	22.413048	0.2717231	1.946663	−0.00507	0.999458	0.54032	1.7262	−0.002
0.7498	0.2502	22.413048	0.2346933	2.259008	−0.11679	0.999531	0.46676	2.0036	−0.046
0.4998	0.5002	22.413048	0.1337381	2.616660	−0.21085	0.999732	0.26608	2.3222	−0.083
0.2498	0.7502	22.413048	−0.0311371	3.169740	−0.24101	1.000059	−0.06199	2.8158	−0.096
0.0000	1.0000	22.413048	−0.2597376	4.066926	−0.16109	1.000514	−0.51758	3.6177	−0.064

3. *Data of Scott.*

$t = 25°$ C.

H_2	CO								
1.000	0.000	24.464548	0.3148116	2.134284	−0.00425	1.090975	0.62605	1.8927	−0.002
0.663	0.337	24.464548	0.2728472	2.576323	−0.12909	1.091051	0.54267	2.2852	−0.051
0.517	0.483	24.464548	0.2186026	2.787221	−0.17281	1.091150	0.43486	2.4729	−0.068
0.331	0.669	24.464548	0.1179137	3.138875	−0.20232	1.091333	0.23464	2.7863	−0.080
0.000	1.000	24.464548	−0.1487955	4.175916	−0.13521	1.091818	−0.29636	3.7119	−0.054

TABLE V.

VALUES OF THE VIRIAL COEFFICIENTS.

Linear combination of R, $A_0^{1/2}$, a, b, c and Lorentz combination of B_0.

1. *Data of Masson and Dolley.*

$t = 24.95°$ C.

Mole fraction		Virial coefficients in normal units				Virial coefficients in units of data			
A	C_2H_4	RT	β_n	$\gamma_n \times 10^2$	$\delta_n \times 10^4$	RT	$\beta_n \times 10^3$	$\gamma_n \times 10^6$	$\delta_n \times 10^9$
0.7517	0.2483	24.460445	−0.8620498	4.667815	0.47570	1.001894	−1.44626	3.2076	0.134
0.4992	0.5008	24.460445	−1.5294073	7.544902	1.83137	1.003176	−2.57246	5.2047	0.518
0.4002	0.5998	24.460445	−1.8410588	9.005288	2.71053	1.003678	−3.09976	6.2214	0.768
0.2918	0.7082	24.460445	−2.2146242	10.851958	3.95694	1.004231	−3.73283	7.5096	1.124
0.0989	0.9011	24.460445	−2.9629179	14.853347	7.05544	1.005213	−5.00388	10.3087	2.012
O_2	C_2H_4								
0.7463	0.2537	24.460445	−0.9163642	5.089956	0.66725	1.001948	−1.53755	3.4983	0.188
0.4996	0.5004	24.460445	−1.5739479	7.891289	2.06594	1.003189	−2.64744	5.4438	0.585
0.4004	0.5996	24.460445	−1.8827671	9.324198	2.95104	1.003691	−3.17006	6.4420	0.837
A	O_2								
0.4999	0.5001	24.460445	−0.3937658	2.963568	0.04479	1.000656	−0.65899	2.0290	0.013

TABLE V.—Concluded.

2. *Data of Verschoyle.*

$t = 20°$ C.

Mole fraction		Virial coefficients in normal units				Virial coefficients in units of data			
H_2	N_2	RT	β_n	$\gamma_n \times 10^2$	$\delta_n \times 10^4$	RT	$\beta_n \times 10^3$	$\gamma_n \times 10^6$	$\delta_n \times 10^9$
0.7498	0.2502	24.054248	0.2635655	2.358238	−0.09854	1.072760	0.52422	2.0918	−0.039
0.4998	0.5002	24.054248	0.1698198	2.713132	−0.17760	1.072988	0.33791	2.4081	−0.070
0.2498	0.7502	24.054248	0.0249750	3.274731	−0.20537	1.073327	0.04973	2.9094	−0.081

$t = 0°$ C.

H_2	N_2								
0.7498	0.2502	22.413048	0.2167852	2.198338	−0.11350	0.999567	0.43117	1.9500	−0.045
0.4998	0.5002	22.413048	0.1098682	2.558896	−0.20456	0.999779	0.21861	2.2712	−0.081
0.2498	0.7502	22.413048	−0.0490227	3.143769	−0.23655	1.000095	−0.09760	2.7930	−0.094

3. *Data of Scott.*

$t = 25°$ C.

H_2	CO								
0.663	0.337	24.464548	0.2495570	2.504863	−0.12511	1.091093	0.49639	2.2221	−0.049
0.517	0.483	24.464548	0.1925723	2.721889	−0.16759	1.091197	0.38311	2.4153	−0.066
0.331	0.669	24.464548	0.0948192	3.097341	−0.19763	1.091375	0.18870	2.7498	−0.078

7. Graphs of the Deviations of the Pressures Calculated by the Beattie-Bridgeman Equation of State for Mixtures from the Observed Values.

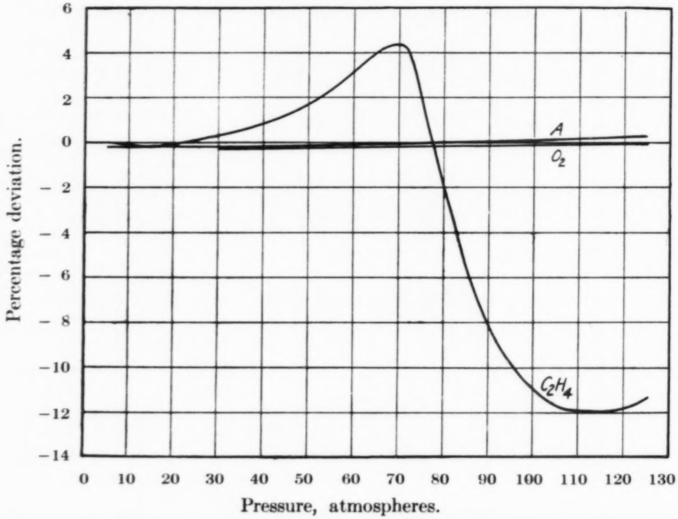

Figure 1. Masson and Dolley: Argon, oxygen and ethylene at 24.95° C.

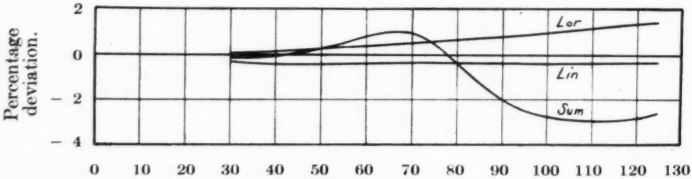

Figure 2. Masson and Dolley: 75.17% argon, 24.83% ethylene at 24.95° C.

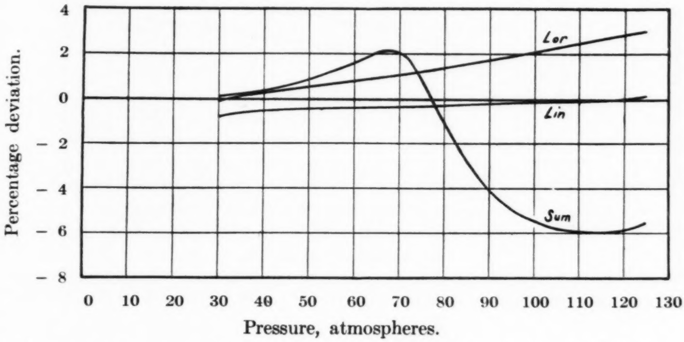

FIGURE 3. Masson and Dolley: 49.92% argon, 50.08% ethylene at 24.95° C.

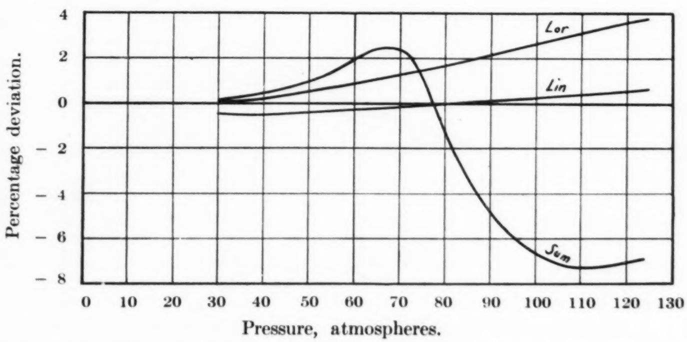

FIGURE 4. Masson and Dolley: 40.02% argon, 59.98% ethylene at 24.95° C.

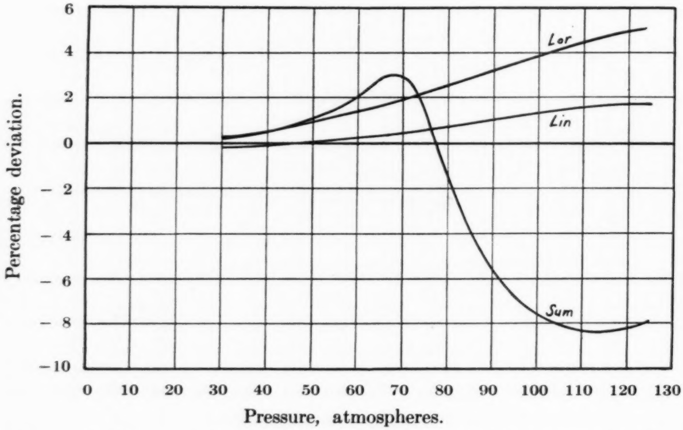

FIGURE 5. Masson and Dolley: 29.18% argon, 70.82% ethylene at 24.95° C.

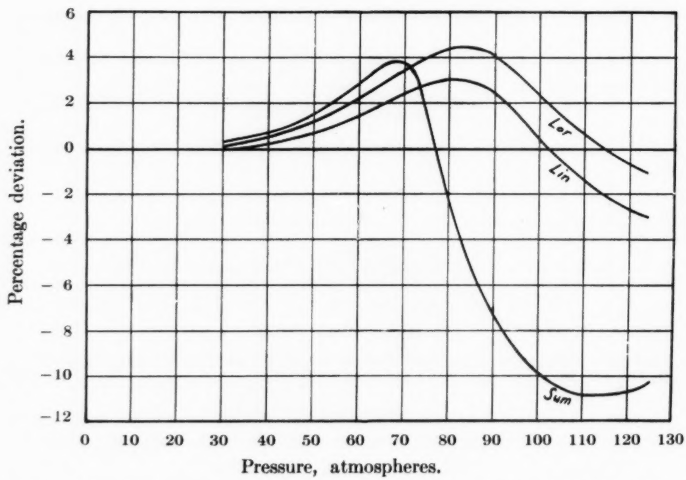

FIGURE 6. Masson and Dolley: 9.89% argon, 90.11% ethylene at 24.95° C.

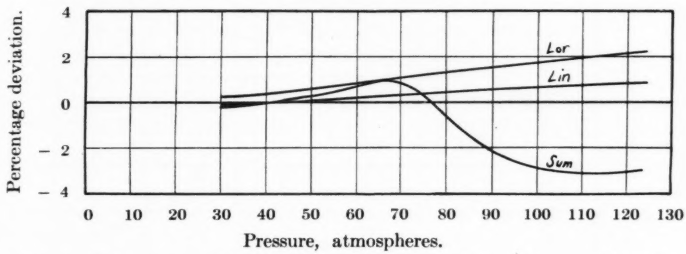

FIGURE 7. Masson and Dolley: 74.63% oxygen, 25.37% ethylene at 24.95°C.

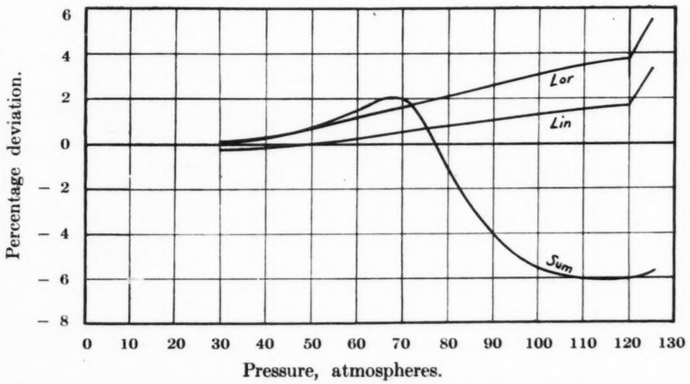

FIGURE 8. Masson and Dolley: 49.96% oxygen, 50.04% ethylene at 24.95° C.

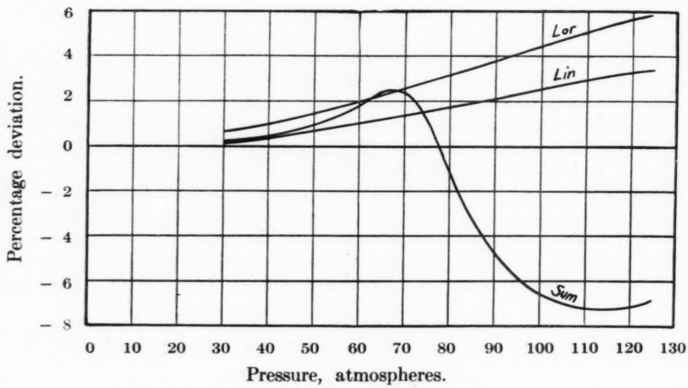

FIGURE 9. Masson and Dolley: 40.04% oxygen, 59.96% ethylene at 24.95° C.

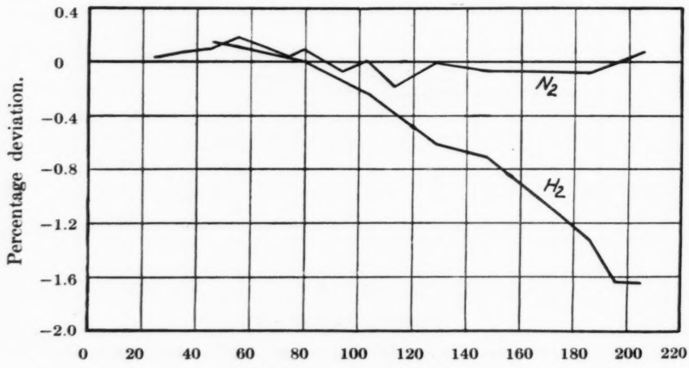

FIGURE 10. Verschoyle: Hydrogen and nitrogen at 20° C.

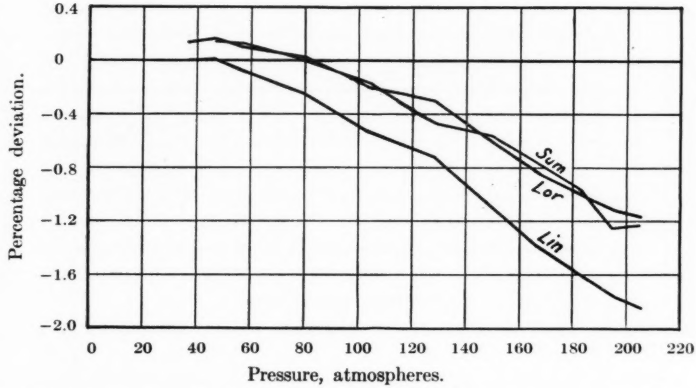

FIGURE 11. Verschoyle: 74.98% hydrogen, 25.02% nitrogen at 20° C.

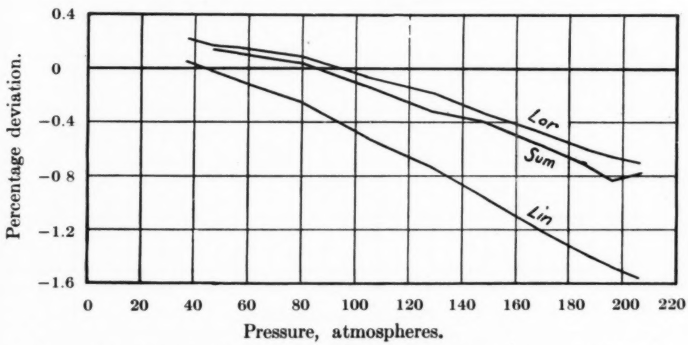

FIGURE 12. Verschoyle: 49.98% hydrogen, 50.02% nitrogen at 20° C.

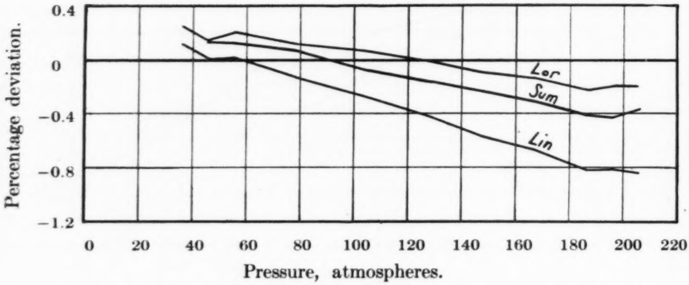

FIGURE 13. Verschoyle: 24.98% hydrogen, 75.02% nitrogen at 20° C.

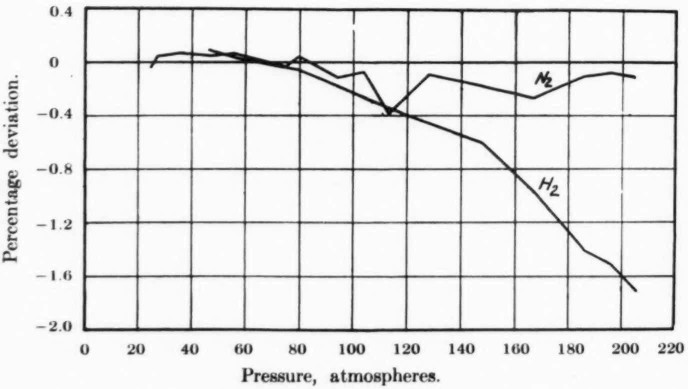

FIGURE 14. Verschoyle: Hydrogen and nitrogen at 0° C.

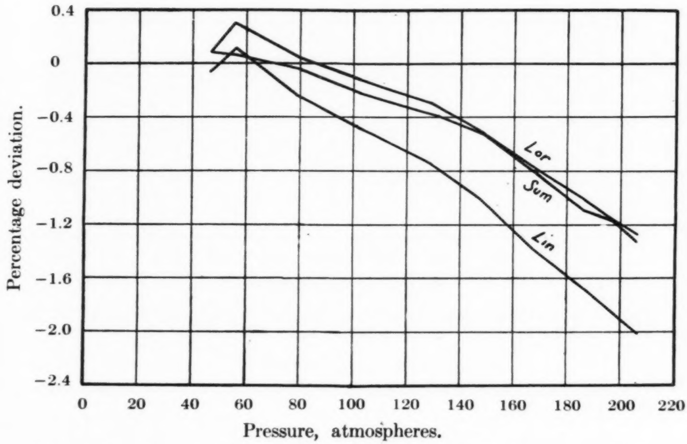

FIGURE 15. Verschoyle: 74.98% hydrogen, 25.02% nitrogen at 0° C.

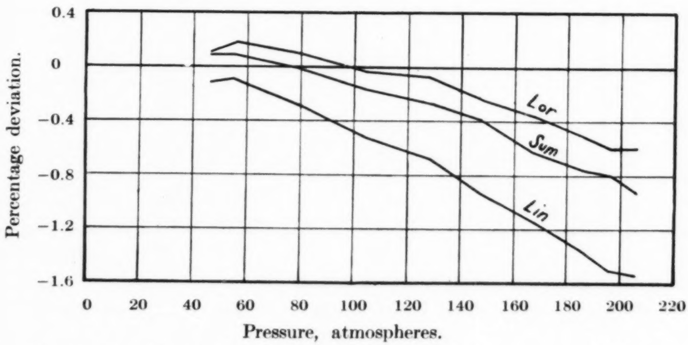

FIGURE 16. Verschoyle: 49.98% hydrogen, 50.02% nitrogen at 0° C.

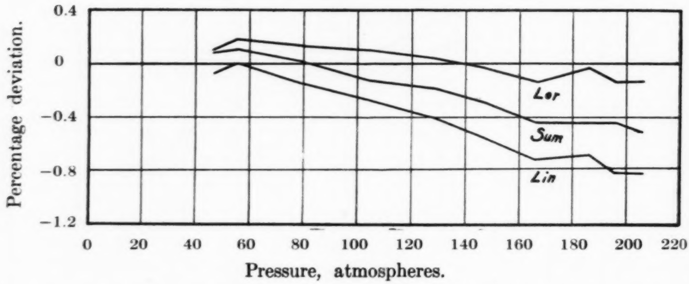

FIGURE 17. Verschoyle: 24.98% hydrogen, 75.02% nitrogen at 0° C.

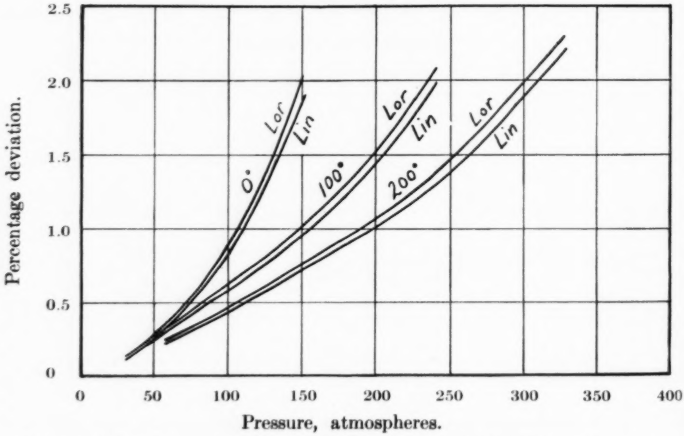

FIGURE 18. Keyes and Burks: 56.66% nitrogen, 43.34% methane at 0°, 100° and 200° C.

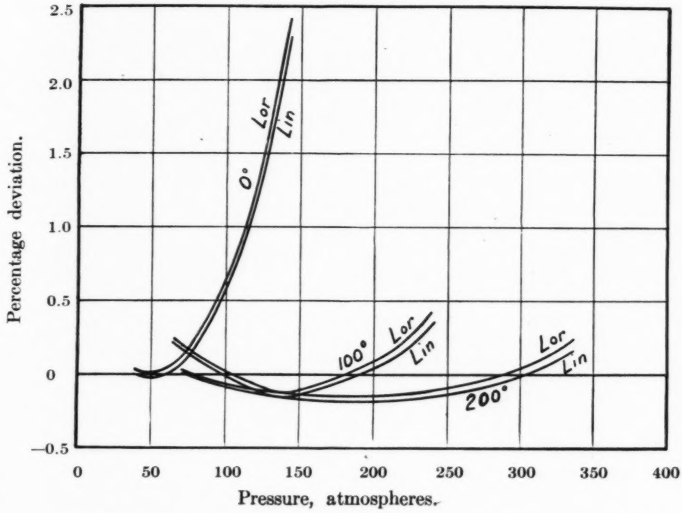

FIGURE 19. Keyes and Burks: 20.46% nitrogen, 79.54% methane at 0°, 100° and 200° C.

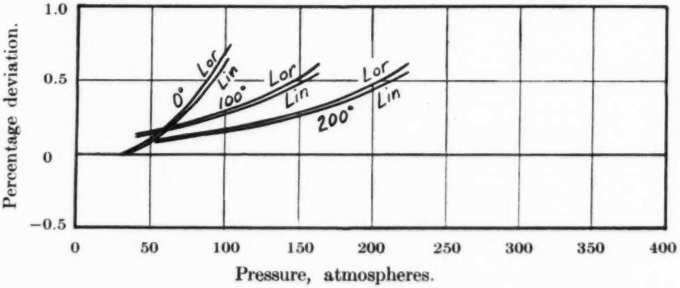

FIGURE 20. Keyes and Burke: 19.46% nitrogen, 80.54% methane at 0°, 100° and 200° C.

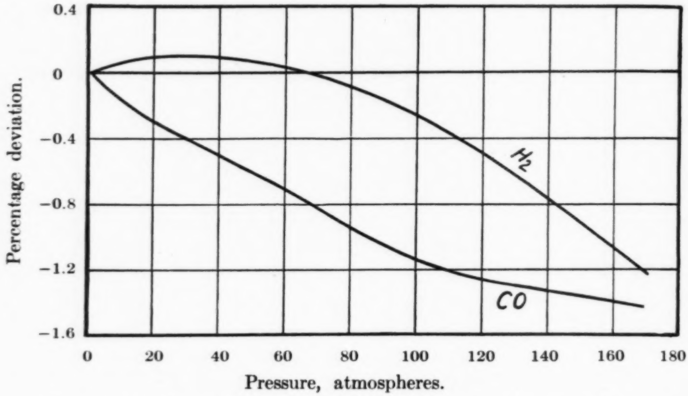

FIGURE 21. Scott: Hydrogen and carbon monoxide at 25° C.

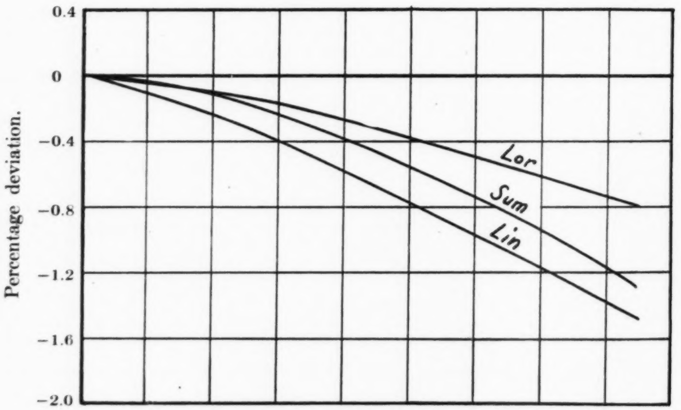

FIGURE 22. Scott: 66.3% hydrogen, 33.7% carbon monoxide at 25° C.

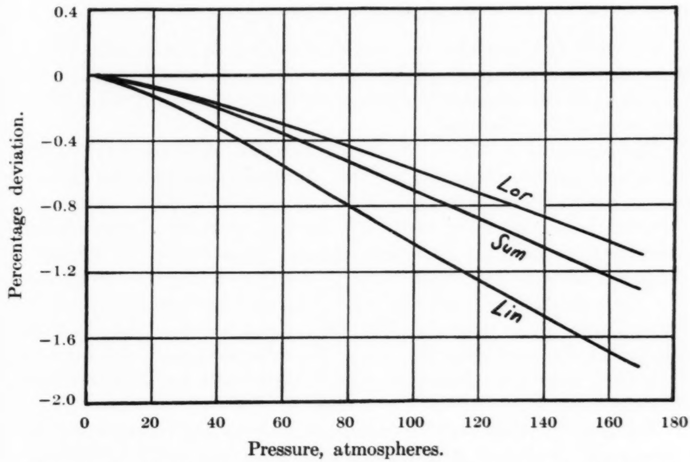

FIGURE 23. Scott: 51.7% hydrogen, 48.3% carbon monoxide at 25° C.

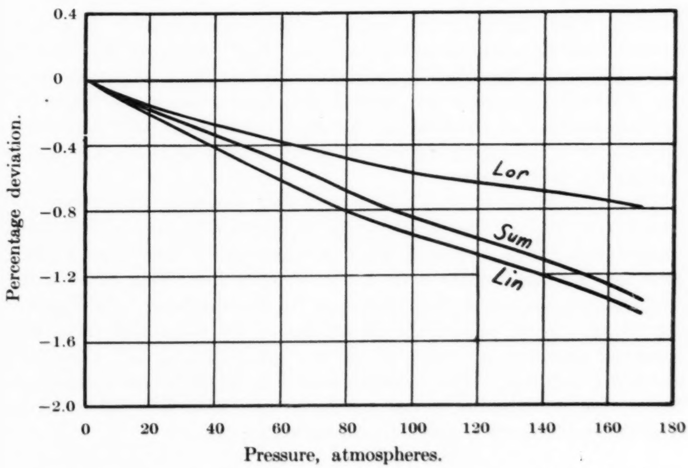

FIGURE 24. Scott: 33.1% hydrogen, 66.9% carbon monoxide at 25° C.

8. Discussion of the Graphs.

We shall first consider the results exhibited in the graphs with a view to determining which of the methods of combination of the constants of the equation of state gives the best representation of the pressures of the mixtures.

The constants a, b and c have in general so small an effect on the calculated pressure that the method of combination used for them is not important; hence throughout the present treatment linear combination is employed for each. Of the two methods of combination that could be used for A_0, linear or linear square root, the former is excluded because this would lead to zero or to negative intercepts for the expansion of gases on mixing at zero pressure; hence in all cases linear square root combination is used for A_0. For B_0 three methods have been proposed: linear, linear square root, and Lorentz. The plots have been drawn to exhibit the results for these methods of combining B_0.

For each mixture there is given two curves one representing the percentage deviation of the calculated from the observed pressure when linear combination is used for B_0 and the other when Lorentz combination for B_0 is used. In each case all of the other constants are combined according to the relations (19). The deviation curves resulting when linear square root combination is used for B_0 would in each case be about as far above the "Lor" curve as the "Lor" curve lies above the "Lin" curve. In the first place we notice that the differences between the results obtained by using the linear or Lorentz method of combination for B_0 are not great and that they increase with increasing differences in the values of B_0 for the gases composing the mixture.

The measurements of Keyes and Burke together with those of Smith and Taylor are the only set that extends over a sufficient temperature range to permit the determination of the values of the equation of state constants for the pure gases from data taken with the same apparatus as that employed for the mixtures. In Figures 18, 19 and 20 are shown the deviations of the calculated from the observed pressures for three of the five temperatures, 50° and 150° not being included. The average deviations for all temperatures and for the entire pressure range are given in Table VI. There is a slight trend in favor of linear combination for B_0.

TABLE VI.

Average Deviations of the Pressures Calculated by the Beattie-Bridgeman Equation of State from the Observed Values for the Nitrogen-Methane Mixtures.

Mole fraction		Average percentage deviation	
N_2	CH_4	Linear B_{0x}	Lorentz B_{0x}
1.0000	0.0000	0.11%	
0.5666	0.4334	.73	0.78%
0.2046	0.7954	.20	.21
0.1946	0.8054	.23	.26
0.0000	1.0000	.07	

For the discussion of the results of Masson and Dolley, of Verschoyle, and of Scott from the standpoint of the methods of combination of constants we are not in so favorable a position since it is necessary to employ values of the constants for the various pure gases determined from the data of other observers. It is generally true that two sets of compressibility data taken by different observers on the same gas do not agree with each other to the same order of accuracy as the consistency of each group of measurements within itself. For this reason the curve labeled "Sum" which is determined by $\Sigma(x_i\%_{0i})$ is added. It is not intended that this curve correct completely for the deviations of the equation of state from the compressibility data on the pure gases, but it is believed that unless otherwise noted weight should be given to the curve when discussing the deviation curves for the mixtures. For reasons given below the curves representing the Masson and Dolley data are not referred to the "Sum" curve; but those for the results of Verschoyle and of Scott are treated from this standpoint.

The values of the constants for ethylene determined[35] from Amagat's data do not give a satisfactory representation of Masson and Dolley's measurements on pure ethylene although they do lead to a good reproduction of the mixture data. This lack of agreement in the case of the pure ethylene may be due in part to the fact that the densities above 70 atmospheres at 25° C. are greater than the critical density and in part to the real disagreement between the data of Amagat and of Masson and Dolley. It will be noticed that the mixture equation gives a fairly good representation of the mixture containing as much as 90% ethylene and this suggests that perhaps there may be an error in the pure ethylene data. In any case it is evident that very little weight can be given the "Sum" curve when discussing the mixture data and hence the curves are compared with the axis representing zero deviation. An examination of the curves given in Figures 2 to 9 from this standpoint shows a trend in favor of linear combination of B_0.

The results of the treatment of the data of Verschoyle and of Scott are given in Figures 10 to 17 and Figures 21 to 24 respectively. In each case the deviation curves for the mixtures are to be compared with that labeled "Sum." There seems to be little choice in the method of combining B_0 for these mixtures since the curve marked "Sum" lies about half way between the "Lin" and "Lor" curves in every case except for the mixture containing 74.98% hydrogen—25.02% nitrogen when it coincides with the "Lor" curve.

The linear square root method of combination for B_0 leads to a deviation curve lying above the "Lor" curve. But the deviation curves resulting when Lorentz combination is used lie almost entirely above the experimental results, and hence linear square root combination for B_0 is not supported.

It is possible that one method of combination will give the best results for one pair of substances and another method for another pair. If however we wish to use one method for all mixtures, the evidence is slightly in favor of linear combination for B_0; and in view of the much greater simplicity of this method of combination it is the one recommended.

It seems reasonable to conclude that the Beattie-Bridgeman equation (18) for gas mixtures together with the method of combination (19) gives a satisfactory over-all correlation of the data for the cases studied, though the agreement may not be within the experimental error in some cases.

The question of whether or not the method of combination (19) reproduces the data on gas mixtures with sufficient accuracy for determining the general thermodynamic properties of mixtures cannot be treated in the present paper. Investigation by Lurie and Gillespie,[12] Gillespie,[35] and Gillespie and Beattie[44] indicate that the method of combination (19) does give satisfactory results in several cases. It is believed that the most severe test of an equation of state for mixtures is the representation of compressibility data. An equation that gives a fair reproduction of the pressure-volume-temperature data on gas mixtures will represent many other thermodynamic properties excellently.

9. Linear Combination of Constants Compared with Dalton's and with Amagat's Law.

The method of combination (19) may be called linear combination of constants. It is of interest to determine whether this method leads to substantially better results than Dalton's law of the additivity of pressures at constant volume and temperature or Amagat's law of the additivity of volumes at constant pressure and temperature.

Lurie and Gillespie,[12] and Keyes and Burks[16] have found that linear combination of constants in the Keyes equation of state gives better results than Dalton's or Amagat's law for mixtures of nitrogen with ammonia and of nitrogen with methane respectively. Gillespie[35] has shown that linear combination of constants in the Beattie-

Bridgeman equation of state gives a much better representation of the expansion of gases on mixing at low pressure than Amagat's law for argon-ethylene, oxygen-ethylene, nitrogen-methane and hydrogen-nitrogen mixtures.

Keyes and Burks do not discuss their compressibility data from the standpoint of Dalton's law of additive pressures; they use the law of "partial pressure" in terms of weight fractions. They also give comparisons (their Figure 1) of the volumes calculated by use of Amagat's law with the observed volumes for two of their mixtures. In Table VII are given the percentage deviations (read from their plot) of the volumes of the mixtures calculated by Amagat's law from the observed volumes; and the percentage deviations of the pressures of the mixtures computed by linear combination of constants in the equation of state from the observed pressures, these latter deviations being determined from our plots 18 and 20. Linear combination of constants gives a better representation of the nitrogen-methane data than Amagat's law; and, since Amagat's law should give better results for these mixtures than Dalton's law, it is safe to conclude that linear combination of constants gives a better representation than Dalton's law.

Masson and Dolley give for all of their mixtures the deviations resulting when Dalton's law and when Amagat's law are used. In Table VIII are given the average percentage deviations of the pressures of the mixtures calculated by Dalton's law from the observed pressures, and of the volumes of the mixture calculated by Amagat's law from the observed volumes. The deviations of the pressures calculated by linear combination of constants from the observed pressure are also given. The Dalton law and Amagat law percentages were obtained by dividing the deviations by the *calculated* pressures or volumes, whereas the linear combination percentage deviation were obtained by dividing by the *observed* pressures in the usual manner. Examination of Table VIII shows that linear combination of constants is far superior to either adding pressures or adding volumes.

Neither Verschoyle nor Scott treated their results from the standpoint of Dalton's or Amagat's law. Calculation for several points shows that for these mixtures linear combination of constants gives the best results but the superiority of this method is not so pronounced as for those mixtures containing ethylene.

TABLE VII.

PERCENTAGE DEVIATIONS RESULTING FROM THE USE OF LINEAR COMBINATION OF CONSTANTS IN THE EQUATION OF STATE AND OF AMAGAT'S LAW FOR THE NITROGEN-METHANE MIXTURES.

Temp., ° C. / Pressure, atm.	Method	0°	100°	200°
		Percentage deviations.		
	A. 56.66% N_2, 43.34% CH_4.			
50	Amagat	1.30%	0.45%	0.25%
	Linear combination	0.25	0.25	0.20
100	Amagat		1.15	0.70
	Linear combination		0.60	0.40
	B. 19.46% N_2, 80.54% CH_4.			
50	Amagat	0.75	0.25	0.15
	Linear combination	0.05	0.10	0.05
100	Amagat		0.70	0.35
	Linear combination		0.30	0.15

TABLE VIII.

Average Percentage Deviations Resulting from the use of Linear Combination of Constants in the Equation of State, Dalton's Law, and Amagat's Law for the Argon-Ethylene and Oxygen-Ethylene Mixtures.

The percentage deviations for linear combination of constants were given for every 5 atmospheres and are referred to the observed pressures; those for Dalton's law and Amagat's law were given for every 10 atmospheres and are referred to the additive pressure or volume.

Mole fraction		Average percentage deviations at 24.95° C. from 30 to 125 atmospheres.		
A	C_2H_4	Dalton's law	Amagat's law	Linear combination
0.7517	0.2483	4.5%	8.0%	0.4%
0.4992	0.5008	6.5	14.5	0.3
0.4002	0.5998	6.3	15.8	0.3
0.2918	0.7082	4.6	16.0	0.8
0.0989	0.9011	3.2	9.1	1.6
O_2	C_2H_4			
0.7463	0.2537	4.4	8.7	0.4
0.4996	0.5004	6.7	14.6	0.9
0.4004	0.5996	5.7	17.3	1.8

10. The Second Virial Coefficient.

Gibby, Tanner and Masson[40] have found a maximum in the second virial coefficient for helium-hydrogen mixtures at 25° C. Using the method of combination of constants (19) we can write the second virial coefficient β_x for a binary mixture in terms of the mole fractions:

$$\beta_x = RT[x_1B_{01} + (1 - x_1)B_{02}] - [x_1A_{01}^{1/2} + (1 - x_1)A_{01}^{1/2}]^2 - \frac{R}{T^2}[x_1c_1 + (1 - x_1)c_2] \quad (22)$$

Differentiating and equating to zero we find that β_x has a maximum or minimum value at

$$x_1 = \frac{1}{2} + \frac{\beta_1 - \beta_2}{2(A_{01}^{1/2} - A_{02}^{1/2})^2} \quad (23)$$

where β_1 and β_2 are the virial coefficients for the pure Gases 1 and 2 respectively. Moreover, this value of x_1 must correspond to a maximum value of β_x since the curvature

$$\left(\frac{d^2\beta_x}{dx^2}\right)_T = -2\,(A_{01}^{1/2} - A_{02}^{1/2})^2 \quad (24)$$

is always negative whatever the values of A_{01} and A_{02}.

The existing experimental data on binary mixtures indicate that the β_x vs. x_1 curve does not exhibit a maximum, except perhaps in certain temperature regions. From equation (23) we see that no maximum will exist for values of x_1 between zero and unity unless the numerical values of the last term of (23) is less than ½. Substitution of the numerical values of the constants for hydrogen and helium into (23) gives a calculated maximum at about 50% hydrogen. The plot given by Gibby, Tanner and Masson indicates a maximum for β_x at about 80% hydrogen. In a later publication,[45] Tanner and Masson "restate the data" of their earlier paper and give a corrected plot which indicates a maximum at about 70% hydrogen. The curvature is so slight that the maximum cannot be located with exactness. The lack of quantitative agreement between the calculated and the observed values of the maximum is probably due to one or both of two causes: (1) Deviation of the equation of state of hydrogen or helium from the data of Gibby, Tanner and Masson on the pure gases, and (2) the fact that these investigators used only two terms of the virial to represent their isotherms, whereas the equation of

state virial contains four terms for hydrogen and three for helium.

Equation (23) calculates a maximum in the β_x curve for hydrogen-nitrogen mixtures at 97% hydrogen for 20° C. but no maximum at 0° C. Verschoyle's curves were drawn without a maximum, but the 20° curve almost admits of a maximum.

Gibby, Tanner and Masson, and Verschoyle each expanded pV in an ascending power series of the pressure but the second coefficient of this expansion should correspond to the β_x of equation (22) divided by RT.

11. Summary.

The Beattie-Bridgeman equation of state (18) has been applied to the calculation of the pressures of gaseous mixtures of argon with ethylene, oxygen with ethylene, hydrogen with nitrogen, nitrogen with methane and hydrogen with carbon monoxide.

The equation of state constants a, b and c, which do not, in general, have a great effect on the calculated pressure were combined linearly with the composition of the mixture. In accordance with the results of several previous investigations, linear square root combination was used for A_0. The relative merits of linear, Lorentz, and linear square root combination for B_0 were studied by the use of deviation curves for all of the mixtures. On the whole, linear combination for B_0 was slightly favored over the Lorentz method, while the linear square root relation gave the least satisfactory results. It is pointed out that there is little theoretical evidence in favor of the Lorentz method.

Linear combination for each of the constants R, $A_0^{1/2}$, a, B_0, b and c of the Beattie-Bridgeman equation of state gives a satisfactory over-all correlation of the compressibility data on gas mixtures, although in some cases the representation of the data may not be within the experimental error.

For all of the mixtures studied, linear combination of the constants of the equation of state gives a much better representation of the experimental data than either Dalton's law or Amagat's law.

It had been experimentally found that certain mixtures of helium and hydrogen have a larger second virial coefficient than the pure gases. The equation of state confirms the existence of such a maximum and predicts a similar phenomenon for other mixtures within certain temperature ranges.

The values of the equation of state constants for nitrogen give a satisfactory representation of the compressibility of carbon monoxide

to 170 atmospheres at 25° C., a result which is not unexpected in view of Langmuir's theory of isosters.

12. References.

[1] van der Waals, "Die Continuität des Gasförmigen und Flüssigen Zustandes," Barth, Leipzig, *1900;* Part II.

[2] van Laar and Lorenz, Zeit. für anorg. und allg. Chem., *145*, 239 (1925).

[3] Keyes, Jour. Amer. Chem. Soc., *49*, 1393 (1927).

[4] Keyes, Amer. Soc. Refrig. Eng. Jour., *1*, 9 (1914); Proc. Nat. Acad. Sci., *3*, 323 (1917).

[5] Gillespie, Jour. Amer. Chem. Soc., *47*, 305 (1925); ibid., *48*, 28 (1926). Physical Review, *34*, 352 (1929); ibid., *34*, 1605 (1929).

[6] De Donder, Comptes Rendus Acad. Sci. Paris, *180*, 1922 (1925). "L'affinité," Gauthier-Villars, Paris, *1927*.

[7] Van Lerberghe, Comptes Rendus Acad. Sci. Paris, *181*, 851 (1925); Bulletin de l'Acad. roy. de Belgique (Classe de Sciences), *14*, 349 (1928). "Le Calcul des Fugacitiés d'une Solution," Marcel Hayez, Bruxelles, *1928*.

[8] Beattie, Physical Review, *31*, 680 (1928); ibid., *32*, 691, 699 (1928); ibid., *34*, 1615 (1929).

[9] Beattie, forthcoming publication.

[10] Dalton, Nicholson's Journal of Science, *5*, 241 (1801); Gilbert's Ann. der Physik, *12*, 385 (1802); ibid., *15*, 1 (1803).

[11] Gibbs, "The Scientific Papers of J. Willard Gibbs," Longmans, Green, and Co., New York, *1906;* Vol. 1, p. 155.

[12] Lurie and Gillespie, Jour. Amer. Chem. Soc., *49*, 1146 (1927).

[13] Amagat, Ann. chim. phys., (5) *19*, 384 (1880); Comptes Rendus Acad. Sci. Paris, *127*, 88 (1898).

[14] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, *1923;* p. 226.

[15] See for instance: Leduc, Comptes Rendus Acad. Sci. Paris, *126*, 218 (1898); Penning, Archives Néerlandaises, III A, *7*, 172 (1923); Comm. Phys. Lab. Univ. Leiden, No. 166; Holborn and Otto, Zeit. für Physik, *23*, 77 (1924).

[16] Keyes and Burks, Jour. Amer. Chem. Soc., *50*, 1100 (1928).

[17] Masson and Dolley, Proc. Roy. Soc., London, *103 A*, 524 (1923).

[18] van der Waals. "Die Continuität"; Vol. I.

[19] See for instance Fowler, "Statistical Mechanics," University Press, Cambridge, *1929;* p. 206.

[20] Berthelot, Comptes Rendus Acad. Sci. Paris, *126*, 1703, 1857 (1898).

[21] Galitzine, Wied. Ann. der Physik, *41*, 770 (1890).

[22] Lorentz, Wied. Ann. der Physik, *12*, 127, 660 (1881).

[23] See for instance Trautz and Emert, Zeit. für anorg. u. allgem. Chem. *150*, 277 (1926); Trautz and Narath, Wied. Ann. der Physik, (4), *79*, 637, (1926); Eucken and Bresler, Zeit. für phys. Chem., *134*, 230 (1928).

[24] Phillips, Jour. of Math. and Physics, *1*, No. 1 (1921); see also Beattie and Bridgeman, Proc. Amer. Acad. Arts and Sci., *63*, 229 (1928).

[25] Beattie, Jour. Amer. Chem. Soc., *51*, 19 (1929).

[26] Beattie and Bridgeman, Jour. Amer. Chem. Soc., *49*, 1665 (1927); ibid., *50*, 3133 (1928). See especially Proc. Amer. Acad. Arts and Sci., *63*, 229 (1928).

[27] Smith and Taylor, Jour. Amer. Chem. Soc., *45*, 2107 (1923); ibid., *48*, 3122 (1926).

[28] Keyes and Burks, Jour. Amer. Chem. Soc., *49*, 1403 (1927).

[29] Lennard-Jones and Cook, Proc. Roy. Soc., London, *115 A*, 334 (1927).

[30] Deming and Shupe, Jour. Franklin Institute, *208*, 389 (1929).

[31] Kleeman, Jour. Franklin Institute, *206*, 511 (1928).

[32] Van Lerberghe, Bulletin d'Acad. roy. de Belgique (Classe de Sciences), (5) *15*, No. 6 (1929).

[33] Eucken and Bresler, Zeit. für phys. Chem., *134*, 230 (1928).

[34] Pollitzer and Strebel, Zeit. für phys. Chem., *110*, 768 (1924).

[35] Gillespie, Physical Review, *34*, 352 (1929). The values of the equation of state constants for ethylene are given by Gillespie, Jour. of Phys. Chem., *33*, 354 (1929).

[36] This work is summarized by Kuenen, "Verdampfund und Verflüssigung von Gemischen," Barth, Leipzig, *1906*.

[37] Kuenen, Verschoyle and van Urk, Comm. Phys. Lab. Univ. Leiden, No. *161*.

[38] Verschoyle, Proc. Roy. Soc., London, *111 A*, 552 (1926).

[39] Bartlett, Cupples and Tremearne, Jour. Amer. Chem. Soc., *50*, 1275 (1928).

[40] Gibby, Tanner and Masson, Proc. Roy. Soc., London, *122 A*, 283 (1929).

[41] Scott, Proc. Roy. Soc., London, *125 A*, 330 (1929).

[42] Beattie and Bridgeman, Jour. Amer. Chem. Soc., *50*, 3151 (1928).

[43] Langmuir, Jour. Amer. Chem. Soc., *41*, 868, 1543 (1919).

[44] Gillespie and Beattie, forthcoming publication.

[45] Tanner and Masson, Proc. Roy. Soc., London, *126 A*, 268 (1930).